X-ray Study of $Cu_{30}Ni_{70}$ Alloy Nanopowders Prepared by Ballmilling

Jithender Ladal, Aparna Pingily, Gopi Krishna Nallacheruvu

Abstract— **$Cu_{30}Ni_{70}$ alloy has been prepared from elemental copper and nickel metal powders by mechanical alloying. Mechanical alloying has been carried out in a Retsch planetary PM 100 ballmill. While preparing the alloy the X-ray diffraction pattern has been recorded after every 10 hours of milling. This procedure has been continued up to 120 hours. At every stage particle size, lattice strain, lattice constant, mean square amplitudes of vibration, Debye-Waller factor and Debye temperature have been determined from X-ray integrated intensities. It has been observed that the formation of $Cu_{30}Ni_{70}$ alloy started after 50 hours of ballmilling. After 100 hours of ballmilling the nickel oxide phase was detected. The Debye characteristic temperature θ_M of the alloy decreases with decreasing particle size.**

***Index Terms*— Mechanical alloying, Cu-Ni alloy, Debye temperature and nanopowders.**

I. Introduction

Cu-Ni alloys have attracted the attention of many researchers due to their anti-corrosion, anti-fouling and electro-catalytic properties. These alloys have high tensile strength and reasonable good wear-resistance [1,2]. This combination of properties makes Cu-Ni alloys suitable for many applications such as resistive and thermo-electric devices or MEMS [3,4]. By properly tanning the composition of the Cu-Ni solid solution, ferromagnetic or non-magnetic properties can be achieved. Ferromagnetic Cu-Ni films find applications in magnetic sensors and activators. The non-magnetic compositions can be used as non-magnetic gap in recording write heads [5]. Some of the properties of Cu-Ni alloys improve remarkably when the alloy is made nanocrystalline [6]. A study of the composition and microstructure of nanodispersed Cu-Ni alloys obtained by different routes from copper and nickel oxides were reported by Canjiano *et al.* [7] Cu-Ni alloy nanopowder particles were also synthesized by chemical alloying technique [8]. The process of ball milling has been successfully employed in the synthesis of wide range of the nanocrystalline magnetic alloys [9-14] such as Cu-Ni-Co alloys. When Co is added to the magnetic Cu-Ni alloy, it leads to attractive magnetic properties due to the coupling of hard and soft magnetic phases and separation of magnetic moments by non-magnetic phases giving rise to spin dependent scattering of conduction electrons at the interfaces as well as within the magnetic properties. The structural and magnetic properties of nanocrystalline Cu-Ni and Cu-Ni-Co alloys prepared by mechanical alloying have been investigated by Mondal *et al.* [15]. They have systematically studied the role of Co addition on the magnetic properties of Cu-Ni alloys prepared by ball milling. The technique of mechanical alloying has also been used to produce super saturated solid solutions even in almost immiscible alloy systems [16, 17]. Yanagitani *et al.* [18] carried out the mechanical alloying of Cu-Ni-Fe powders using a low-energy ball mill and they reported the formation of super saturated solid solution. Sang-ho Kang and Tae-hyun Nam [19] have prepared Ti-Ni and Ti-Ni-Cu shape memory alloy powders by ball milling method under various rotating speeds and periods of milling time. Microstructures and transformation behavior of Ti-Ni-Cu shape memory alloy powders fabricated by ball milling method have been investigated by Sang-ho Kang *et al.* [20]. The character of dislocation structure evaluation in nanocrystalline fcc Ni-Co alloys prepared by high-energy mechanical milling has been studied by Salimon *et al.* [21]. They have shown that high energy ball milling results in the formation of nanocrystalline state in the fcc Ni-Co alloys. It is clear from above discussion that though there is some work on the preparation of Ni-Cu alloys, it is interesting to study the process of formation of alloy and the effect of ball milling on the lattice dynamical parameters like amplitudes of vibration, Debye-Waller factor and Debye temperature of Ni-Cu alloys. In the present work, we have made an attempt to synthesize $Cu_{30}Ni_{70}$ alloy nanopowders and study the effect of ball milling on thermal parameters of $Cu_{30}Ni_{70}$ alloy.

II. Experimental

$Cu_{30}Ni_{70}$ alloy has been prepared from elemental Cu (99.98 wt.% purity) and Ni (99.98 wt.% purity) metal powders by mechanical alloying. Blends of elemental powders with particle size less than 100μm having composition (wt.%) of $Cu_{30}Ni_{70}$ have been ball milled in a Retsch Planetary PM 100 ball mill. The ball mill has been operated at 300 rpm using tungsten carbide vial and balls (10 mm diameter) up to 50 hours of milling and balls (5 mm diameter) up to 120 hours of milling with a ball to powder ratio of 10:1. About 30-40 ml. of acetone was added to the powder blend to prevent agglomeration of powders. Ball milling was continued up to 120 hours as further continuation of ball milling revealed no significant change in the X-ray diffraction pattern of the powder blends. In order to avoid an increase in the vial temperature, the milling procedure was periodically interrupted for about 30 minutes to 1 hour for every hour. The interval of interruption was more after 70 hours of milling. After ball milling, the milling vessel was left to cool for every hour. After each spell of 10 hours of milling, X-ray diffractograms have been recorded to observe the formation

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of the alloy. X-ray diffraction (XRD) patterns of $Cu_{30}Ni_{70}$ alloy for different milling hours (0,10,40,50,70,80,90,100,110 and 120 hours) are given in Fig. 1. About four reflections have been recorded in each case. The integrated intensities of the reflections have been measured with a JEOL JDX 8 P upgraded X-ray diffracometer fitted with a NaI (Tl) scintillation counter using filtered CuKα radiation at room temperature and the intensities have been corrected for thermal diffuse scattering effect by the method suggested by Chipman and Paskin [22].

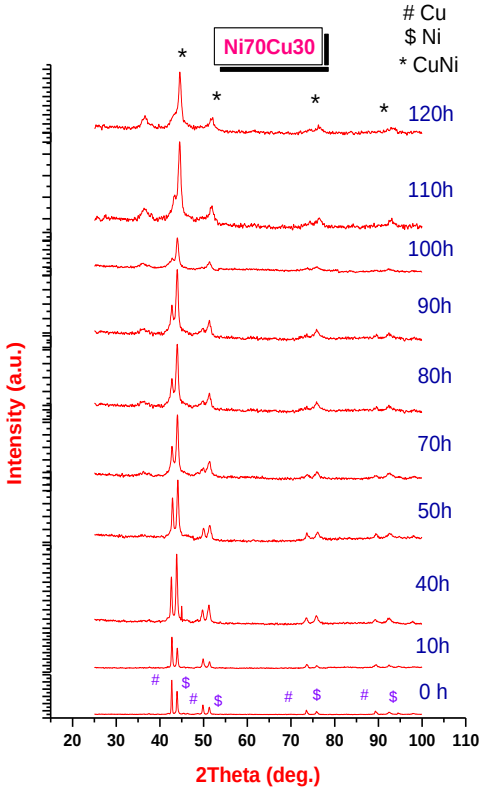


Figure 1. XRD patterns of $Cu_{30}Ni_{70}$ alloy powders for different milling hours from 0h to 120h respectively

III. Analysis of Data

Cu, Ni and $Cu_{30}Ni_{70}$ alloy have fcc structure. The integrated intensity of the Bragg reflection is given as

$$I_o = CL_pJF_T^{\,2} \qquad (1)$$

where L_p is the Lorentz polarization factor, J the multiplicity factor, F_T the structure factor and C is a constant. The structure factor F_T in terms of the structure factor F for the static lattice is given as

$$F_T = F\, e^{-B(\sin\theta/\lambda)^2} \qquad (2)$$

where B is the Debye-waller factor,θ the Bragg angle and λ the wavelength. We can write Eq. (1), as

$$I_o = I_c\, e^{-B(\sin\theta/\lambda)^2} \qquad (3)$$

where I_c is the intensity corresponding to the static lattice and is given as

$$I_c = L_pJF^2 \qquad (4)$$

For fcc metals and alloys, the structure factor F is given as

$$F = 4f \qquad (5)$$

f being the atomic scattering factor. The structure factors are calculated from the atomic scattering factor given by Cromer and Waber [23] and corrected for anomalous dispersion [24]. From Eq. (3), log (I_o/I_c) is linearly related to $(\sin\theta/\lambda)^2$. From a least-square treatment of data, the Debye-Waller factor B can be determined, from the Debye-Waller theory [25].

$$B = 8\pi^2 < u^2 > \qquad (6)$$

For a cubic crystal, $< u^2 >$ is the mean-square amplitudes of vibration. Further, B can also be expressed as $B = (6h^2/mk\theta_M)$ W(x) (7)

where m is the mass , θ_M the Debye temperature and h and k are the Planck and the Boltzmann constants respectively. The function W(x) is given by

$$W(x) = [\phi(x)/x + (1/4)] \qquad (8)$$

wher $x=\theta_M/T$, T is the temperature of the crystal and ϕ(x) is the Debye function. The values of W(x) for a wide range of x can be obtained from Benson and Gill tables [26].

IV. Results and Discussion

Fig. 1. presents the X-ray diffraction patterns of $Cu_{30}Ni_{70}$ alloy powders ball milled for different periods of time. For the sake of comparison the XRD patterns of unmilled powder is also presented in Fig. 1. The XRD pattern of unmilled powder contains peaks pertaining to Cu (fcc) and Ni (fcc) separately. As the milling progressed, the peaks, though they were prominent, they started getting gradually broadened. It was observed that for all reflections the intensity of characteristic copper lines decreased gradually as the duration of the milling increased. The extent of decrease in the intensity of reflections of copper was more pronounced after 70 hours of ball milling indicating the beginning of formation of $Cu_{30}Ni_{70}$ alloy. As milling continues, it was observed that the intensities of characteristic nickel reflections increased indicating the gradual diffusion of Cu into the Ni lattice for the formation of $Cu_{30}Ni_{70}$ solid solution. Up to 50 hours there is no formation of $Cu_{30}Ni_{70}$ alloy solid solution, revealing that the time is insufficient for the diffusion to occur. At 70 hours, solid solution starts to form. The gradual broadening of peaks indicates the decrease in particle size and increased strain.

These changes are shown in Fig. 2 for the reflections (1 1 1) of Cu and Ni.

The lattice constant, amplitudes of vibration, Debye-Waller factor and Debye temperature for $Cu_{30}Ni_{70}$ alloy have been determined from X-ray integrated intensities. Lattice parameters of $Cu_{30}Ni_{70}$ solid solution have been calculated for different periods of milling time from standard procedures. A plot of the change in average lattice constant as a function of milling time is shown in Fig. 3. No systematic change in lattice parameter has been observed with milling time. This could be due to almost identical lattice parameters for Ni and Cu.

The XRD patterns shown in Fig. 1. exhibit a significant broadening of the peaks from the milling time of 50 h onwards due to the refining of particle size and increase of internal lattice strains. After 100 hours of milling, the nickel oxide (NiO) phase was detected. As pointed out earlier, the formation of $Cu_{30}Ni_{70}$ alloy started at about 70h of milling. Hence, the particle size and strain in $Cu_{30}Ni_{70}$ alloy have

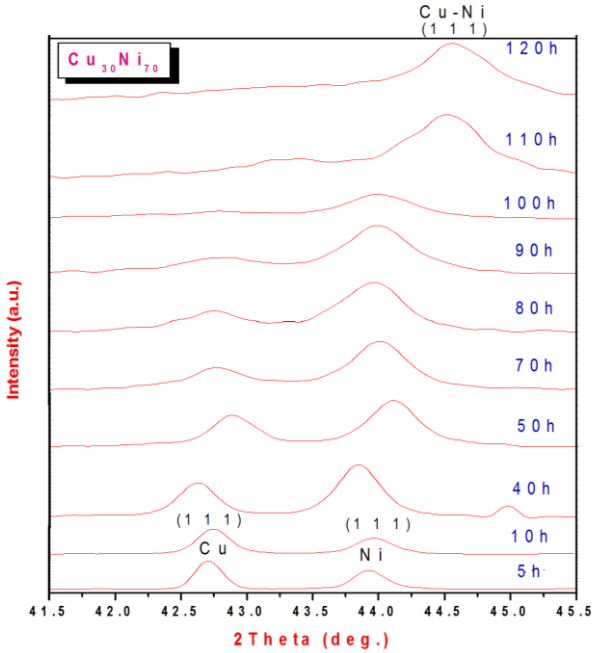


Figure 2. The Gradual merging of (1 1 1) peak of Cu in (1 1 1) peak of Ni

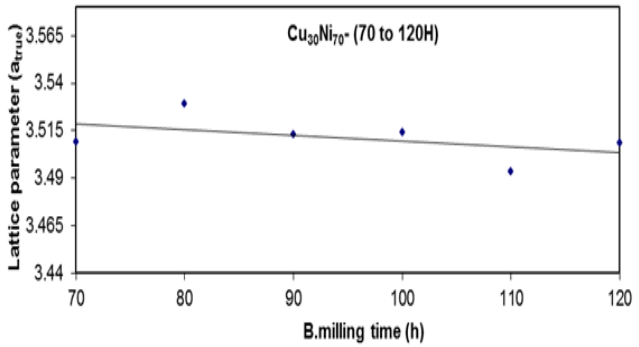


Figure 3. A plot of the change in lattice constant as a function of milling time.

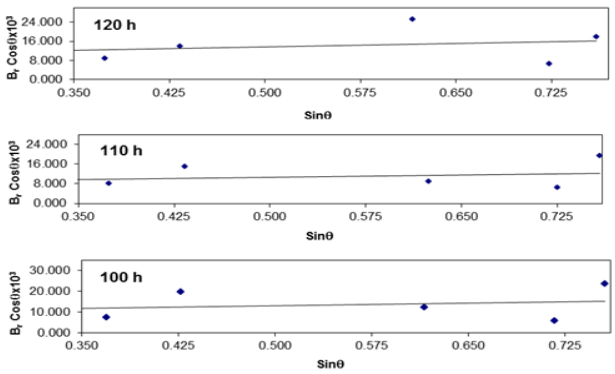
been determined for 70, 80, 90, 100, 110 and 120 hours of milling using the Hall-Williamson formula[27]. The estimation of particle size has been made following Hall-Williamson method [27]. In the present work, the particle size has been determined by measuring the integrated widths of the diffraction peaks rather than half-widths. After eliminating the instrumental broadening effects, the particle size has been determined using the equation,

$$B_r \cos\theta = k\lambda/D + \varepsilon \sin\theta \qquad (9)$$

Where B_r is the peak broadening due to crystallite size and ε the lattice strain, k the shape factor usually taken as 1.0 and D the crystallite size in nanometers, θ and λ are the Bragg angle and the wavelength of incident X-ray beam in nm. The Hall-Williamson plots have been shown for $Cu_{30}Ni_{70}$ alloy for different periods of milling time in Fig. 4. The variation of particle size (D) and lattice strain (ε) as a function of milling time has been shown in Fig. 5. As can be seen from Fig. 5. during the early stage of milling the particle size decreases rapidly and becomes gradually smaller with increasing milling time and reaching a final value of about 17 nm with lattice strain (ε) increasing with milling time.

The analysis of the data for the determination of Debye-Waller factors (B), Debye temperatures (Θ_M) and mean square amplitudes of vibration $\langle u^2 \rangle$ was discussed in section 3. The results obtained for $\langle u^2 \rangle$, Θ_M and B for different milling hours of $Cu_{30}Ni_{70}$ alloy are summarized in Table 1. The variation of Debye-Waller factor of $Cu_{30}Ni_{70}$ alloy for different particle sizes is shown in Fig. 6. It can be observed from the Table 1 that the Debye-Waller factor increases with decrease in particle size. The increase of Debye-Waller factor with the decrease of particle size could be due to the softening of the thermal vibrations of the atoms at the free surface as evidenced from the values of amplitudes of vibration given in Table 1. The increase in the values of Debye-Waller factor causes a decrease in the Debye temperature and hence, as can be seen from Table 1 there is a systematic decrease in the values of Debye temperature with particle size. The values of Debye temperature obtained for $Cu_{30}Ni_{70}$ alloy nanoparticles have been compared with the values obtained from a model proposed by Raghuvesh Kumar and Munish Kumar [28]. Raghuvesh kumar and Munish kumar [28] proposed a model to study the size dependence of Debye temperature for nanoparticles by considering the spherical shape for the particles. The equation given by them is,

$$\theta_{Dn} = \theta_{Db} [1- 2d/D]^{1/2} \qquad (10)$$



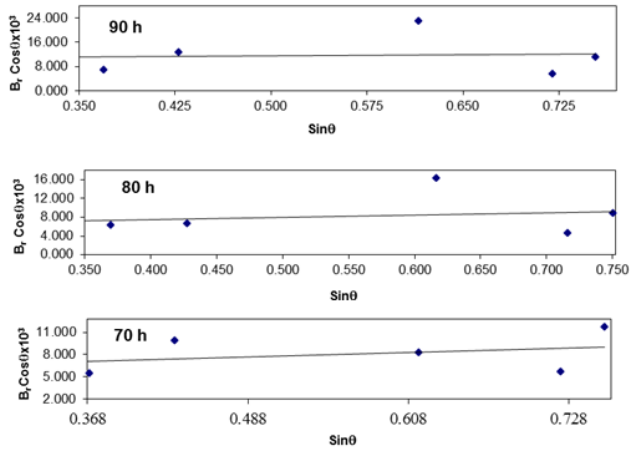


Figure 4. The Hall-Williamson plots for $Cu_{30}Ni_{70}$ alloy for different periods of milling time.

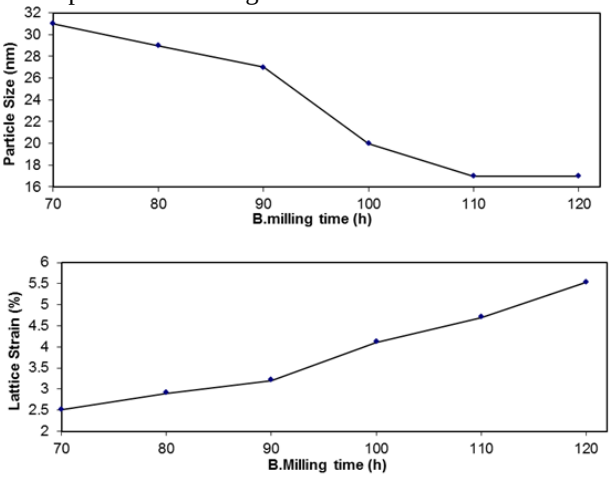


Figure 5. The variation of particle size (D) and lattice strain (ε) as a function of milling time for $Cu_{30}Ni_{70}$ alloy.

TABLE 1. The results obtained for $<u^2>$, θ_M and B for different milling hours of $Cu_{30}Ni_{70}$ alloy.

Milling Time (h)	Particle Size (nm) HW	Lattice Strain (%)	u^2 (Å^2)	B (Å^2)	θ_M (K)
70	31	2.51	0.00365(13)	0.28(01)	459(18)
80	29	2.90	0.00355(14)	0.28(01)	435(19)
90	27	3.20	0.00477(11)	0.37(09)	399(15)
100	20	4.11	0.00676(08)	0.53(07)	333(12)
110	17	4.7	0.00683(12)	0.53(09)	330(16)
120	17	5.53	0.00706(07)	0.55(05)	324(10)

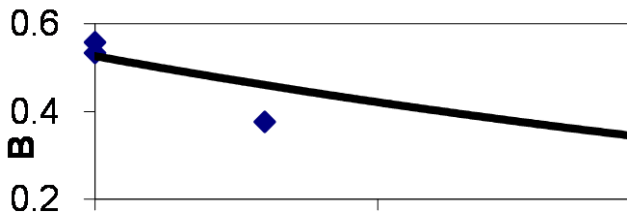


Figure 6. The variation of Debye-Waller factor of $Cu_{30}Ni_{70}$ alloy with different particle size.

where θ_{Dn} is the Debye temperature of nanomaterial, θ_{Db} the Debye temperature of corresponding bulk material, d is the diameter of the atom and D the diameter of nanosolid. The size dependence of Debye temperature in the present work and size dependence from model calculations have been shown in Fig. 7. The large lattice strains produced in $Cu_{30}Ni_{70}$ alloy, during high-energy ballmilling, cause static displacement of atoms in the lattice giving rice to static component of the Debye-Waller factor. The static component of the Debye-Waller factor increases with lattice strain, consequently, the measured values of Debye-Waller factors of particles prepared by ballmilling increase faster than the corresponding strain free particles as the particle size reduces. The enhancement in the value of Debye-Waller factor causes a reduction in the value of Debye temperature and hence, in the present work, the decrease in the values of Debye temperatures shown in Fig. 7. began at slightly larger particle size than the values predicted by the equation proposed by Raghuvesh Kumar and Munish Kumar.

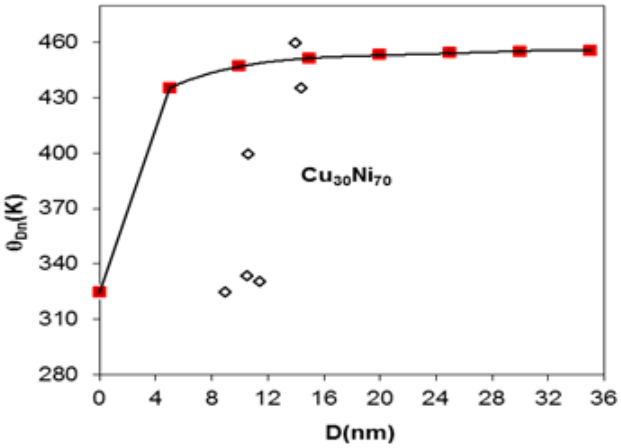


Figure 7. The size dependence of Debye temperature of Cu30Ni70 alloy.

V. Conclusion

The formation of $Cu_{30}Ni_{70}$ alloy started after 50 hours of ballmilling. After 100 hours of ballmilling the nickel oxide (NiO) phase was detected. No systematic change in the lattice parameter of $Cu_{30}Ni_{70}$ alloy has been observed. This could be due to almost identical lattice parameters for Cu and Ni. The effect of particle size on the thermal properties of $Cu_{30}Ni_{70}$ nanopowders has been studied.

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